APPENDIX A

Additional Background Information

Appendix A1: Background on **DNAPL** Contamination

Appendix A2: **Contaminants** Most Frequently Reported in Ground Water at CERCLA NPL Sites

Appendix A3: Examples of **In-Situ** Treatment Technologies

Appendix A4: Definition and Discussion of **Pulsed Pumping**

Appendix A1: Background on DNAPL Contamination

<u>**DNAPL Background**</u>

A **nonaqueous phase liquid (NAPL)** is a chemical that is a liquid in its pure form, which does not readily mix with water but does slowly dissolve in water. **Dense NAPLs (DNAPLs)** sink while **light NAPLs (LNAPLs)** float in water. When present in the subsurface NAPLs slowly release vapor and dissolved phase contaminants, resulting in a zone of contaminant vapors above the water table and a plume of dissolved contaminants below the water table. The term NAPL refers to the undissolved liquid phase of a chemical or mixture of compounds and not to the vapor or dissolved phases. NAPLs may be present in the subsurface as either **"free-phase"** or as **"residual-phase."** The free-phase is that portion of NAPL that can continue to migrate and which can flow into a well. The residual-phase is that portion trapped in pore spaces by capillary forces, which can **not** generally flow into a well or migrate as a separate liquid. Both residual and free-phase NAPLs are sources of vapors and dissolved contaminants.

LNAPLs tend to pose less of a cleanup problem than DNAPLs. The most common LNAPLs are petroleum fuels, crude oils and related chemicals, which tend to be associated with facilities that refine, store or transport these liquids. Since LNAPLs tend to be shallower, are found at the water table and are associated with certain facilities, they are generally easier to locate and clean up from the subsurface than DNAPLs.

DNAPLs pose much more difficult cleanup problems. These contaminants include chemical compounds and mixtures with a wide range of chemical properties, including chlorinated solvents, creosote, coal tars, PCBs, and some pesticides. Some DNAPLs, such as coal tars, are viscous chemical mixtures that move very slowly in the subsurface. Other DNAPLs, such as some chlorinated solvents, can travel very rapidly in the subsurface because they are heavier and less viscous than water. A large DNAPL spill not only sinks vertically downward under gravity, but can spread laterally with increasing depth as it encounters finer grained layers. These chemicals can also contaminate more than one aquifer by penetrating fractures in the geologic layer which separates a shallower from a deeper aquifer. Thus, large releases of DNAPLs can penetrate to great depths and can be very difficult to locate and clean up.

The contamination problem at DNAPL sites has two different components, as shown in **Figures A1-1 and A1-2**, the:
  * DNAPL zone, and the
  * Aqueous contaminant plume.

The **DNAPL zone** is that portion of the subsurface where immiscible liquids (free-phase or residual DNAPL) are present either above or below the water table. Also in the DNAPL zone, vapor phase DNAPL contaminants are present above water table and dissolved phase below water table. The **aqueous contaminant plume** is that portion of the contaminated ground water surrounding the DNAPL zone where aqueous contaminants derived from DNAPLs are dissolved in ground water (or sorbed to aquifer solids) but immiscible liquids are **not** present. Depending on the volume of the release and subsurface geology, the DNAPL zone may extend to great depths and over large lateral distances from the entry location, as discussed above.

Appendix A1: Background on DNAPL Contamination (continued)

Planning of site investigation and remedial activities at sites with subsurface DNAPLs should include certain precautions, to minimize the potential for further DNAPL migration resulting from such activities. Further detail on characterization of DNAPL sites is provided in EPA, 1994 and in Cohen and Mercer, 1993 (see below).

<u>**DNAPL References**</u>

Additional information concerning DNAPL contamination can be obtained from the following references:

Cohen, R.M., and J.W. Mercer, 1993.   <u>DNAPL Site Evaluation</u>, C.K. Smoley, Boca Raton, FL, 1993; and EPA/600/R-93/022, February 1993.

EPA, 1991. "Ground Water Issue: Dense Nonaqueous Phase Liquids," OSWER Publication EPA/540/4-91-002, March 1991.

EPA, 1992a. "Estimating Potential for Occurrence of DNAPL at Superfund Sites," OSWER Publication 9355.4-07FS, January 1992.

EPA, 1992b. "Dense Nonaqueous Phase Liquids -- A Workshop Summary, Dallas, Texas, April 16-18, 1991," Office of Research and Development Publication EPA/600/R-92/030, February 1992.

EPA, 1992c. "Considerations in Ground-Water Remediation at Superfund Sites and RCRA Facilities - Update," OSWER Directive 9283.1-06, May 27, 1992.

EPA, 1993b. "Guidance for Evaluating Technical Impracticability of Ground-Water Restoration," OSWER Directive 9234.2-25, EPA/540-R-93-080, September 1993.

EPA, 1994. "DNAPL Site Characterization," OSWER Publication 9355.4-16FS, EPA/540/F-94/049, September 1994.

Appendix A2: Contaminants Most Frequently Reported in Ground Water at CERCLA NPL Sites [1]

Organic Contaminants:

Rank	Organic Contaminants (Other Names)	Chemical[2] Group	Halo-[2] genated?	DNAPL?[3]	No.[1] Sites
1	Trichloroethylene, 1,1,2- (TCE)[cs]	Volatile	Yes	Yes	336
2	Tetrachloroethene (perchloroethene; PCE)[cs]	Volatile	Yes	Yes	170
3	Chloroform (trichloromethane)[cs]	Volatile	Yes	Yes	167
4	Benzene[pf]	Volatile	No	No	164
5	Toluene[pf]	Volatile	No	No	159
6	Trichloroethane, 1,1,1- (methyl chloroform; 1,1,1-TCA)[cs]	Volatile	Yes	Yes	155
7	Polychlorinated biphenyls	PCB	Yes	Yes	139
8	Trans-Dichloroethylene, 1,2- (trans-1,2-DCE)[cs]	Volatile	Yes	Yes	107
9	Dichloroethane, 1,1- (1,1-DCA)[cs]	Volatile	Yes	Yes	105
10	Dichloroethene, 1,1- (vinylidene chloride; 1,1-DCE)[cs]	Volatile	Yes	Yes	95
11	Vinyl chloride (chloroethylene)[cs]	Volatile	Yes	No	82
12	Xylene[pf]	Volatile	No	No	76
13	Ethylbenzene[pf]	Volatile	No	No	68
14	Carbon tetrachloride (tetrachloromethane)[cs]	Volatile	Yes	Yes	68
15	Phenol	Semivol.	No	No	61
16	Methylene chloride (dichloromethane)[cs]	Volatile	Yes	Yes	58
17	Dichloroethane, 1,2- (ethylene dichloride; 1,2-DCA)[cs]	Volatile	Yes	Yes	57
18	Pentachlorophenol (PCP)	Semivol.	Yes	Yes	53
19	Chlorobenzene (benzene chloride)[cs]	Volatile	Yes	Yes	48
20	Benzo(A)Pyrene	Semivol.	No	Yes	37

Appendix A2: Contaminants Most Frequently Reported in Ground Water at CERCLA NPL Sites (continued)[1]

Inorganic Contaminants:

Rank	Inorganic Contaminants	No.[1] Sites
1	Lead	307
2	Chromium and compounds	215
3	Arsenic	147
4	Cadmium	127
5	Mercury[4]	81
6	Copper and compounds	79
7	Zinc and compounds	73
8	Nickel and compounds	44
9	Cyanides (soluble salts)	39
10	Barium	37

NOTES:

[1]   Number of CERCLA National Priorities List (NPL) sites for which the chemical was reported in ground water as a contaminant of concern in the Superfund Site Assessment, for either proposed or final NPL sites. This data was obtained from the Superfund NPL Assessment Program (SNAP) data base, as of August 30, 1994. At that time total of 1294 sites were listed on the NPL (64 proposed and 1230 final).

[2]   Classification of organic contaminants as volatile, semivolatile, PCB, or pesticide; and as halogenated or nonhalogenated is from EPA Publication, "Technology Screening Guide for Treatment of CERCLA Soils and Sludges," EPA/540/2-88/004, September 1988.

[3]   Classification of whether or not a chemical is a dense nonaqueous phase liquid (DNAPL) in pure form is from Cohen and Mercer, 1993 (see References).

[4]   In pure form mercury is also a DNAPL.

[cs]   These organic contaminants are chlorinated solvents. A total of 12 are listed.

[pf]   These organic contaminants are constituents of petroleum fuels. A total of four are listed.

Appendix A3: Examples of In-Situ Treatment Technologies [1]

I. Enhanced Recovery Methods	Treatment Agents (and process type)	Agent Delivery Methods
Recirculation/flooding:		
- Water flooding (physical)	- Water - Heated water	- Injection wells - Injection wells
- Steam flooding (physical)	- Steam	- Injection wells
- Chemical flooding [2] (chemical)	- Surfactants - Solvents - Redox agents	- Injection wells - Injection wells - Injection wells
- Nutrient flooding [2] (biological)	- Nitrate - Other	- Injection wells
Thermal enhanced recovery:		
- Radio frequency	- Heat	- Electrodes in wells
- Electrical resistance (AC or DC)	- Heat	- Electrodes in wells
Enhancement of secondary permeability:		
- Induced fracturing with water or or air pressure (physical)	Not applicable	Not applicable
Other methods:		
- Electromigration (electrical)	- Electric current	- Electrodes in wells

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NOTES:

[1]   List of technologies and technology status is from EPA, 1993h (see References section of guidance).

[2]   Chemicals or nutrients for micro-organisms, respectively, are added to reinjection water.

Appendix A3: Examples of In-Situ Treatment Technologies (continued)[1]

II. In-situ Treatment Processes	Treatment Agents	Agent Delivery Methods
Physical/chemical treatment:		
- Volatilization and oxygen enhancement by **air sparging**	- Air	- Injection wells - **Permeable walls/gates** [3]
- Reductive dehalogenation by metal catalysts (abiotic)	- Iron filings - Other agents	- **Permeable walls/gates** [3]
Biological treatment:		
- Oxygen enhancement of aerobic organisms (also includes air sparging, above)	- Hydrogen peroxide - Oxygen/surfactant (microbubbles)	- Injection wells[4] - Injection wells[4]
- Nutrient enhancement of aerobic organisms	- Nitrate - Other	- Injection wells[3]
- Nutrient enhancement of anaerobic organisms to produce enzymes that degrade contaminants (cometabolism)	- Methane - Other	- Injection wells
- Sequential anaerobic-aerobic treatment	- Methane and/or Oxygen	- Injection wells

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NOTES:

[3]   In permeable treatment walls/gates, treatment agents are added with trench backfill materials or are injected via perforated pipes placed in the backfill. These walls are placed in the subsurface across the natural flow path of the contaminant plume. They can be combined with impermeable flow barriers in a "funnel and gate" arrangement, in which flow is directed through the treatment walls/gates.

[4]   Use of permeable treatment walls/gates to deliver treatment agents for these methods may also be feasible.

Appendix A4: Definition and Discussion of Pulsed Pumping

<u>**Pulsed Pumping**</u>

In pulsed pumping, some or all extraction pumps are turned off and then back on for specified periods of time (e.g., one or more monitoring periods). The on and off cycles can be continued or the extraction and treatment remedy can be returned to continuous pumping. Although not widely used in remedies to date, this method may be effective in **enhancing the recovery of contaminants from the aquifer** . Pulsed pumping can recover contaminants located in the following portions of the aquifer that are relatively unaffected during pumping:

- Upper portions of the aquifer that have been dewatered by pumping, and

- Zones with minimal ground-water flow during pumping (flow stagnation zones).

Pulsed pumping **may** also enhance contaminant recovery for aqueous phase contaminants that are sorbed to the aquifer matrix. Therefore, pulsed pumping can be initiated as a **post-construction refinement** of an extraction and treatment remedy (see Section 2.4), when an evaluation of remedy performance indicates that this technique may increase the recovery of contaminants from the aquifer.

Pulsed pumping can also be used as a method of evaluating the effectiveness of an extraction and treatment remedy and/or the effectiveness of source control actions.   For example, if contaminant levels increase substantially when pumping is stopped, it is an indication that contaminants continue to be derived from source materials, and that additional remedial measures (e.g., source control/removal) may be necessary. These source materials could include aqueous contaminants sorbed to aquifer solids in finer-grained aquifer layers, NAPLs (refer to Appendix A1), contaminated soils, or other sources.

Pulsed pumping should generally **not be initiated** until after sufficient monitoring data has been obtained from continuous pumping to establish a statistically valid performance trend. Also, the influence of pulsed pumping on plume containment should be considered; and extraction wells used primarily for containment (i.e, at plume leading edge) should generally not be pulsed .

APPENDIX B

ROD Language Examples For Selected Remedy

Appendix B1: Phased Implementation of Ground-Water Remedy

Appendix B2: Phased Implementation of **Extraction Component** of Remedy at a DNAPL Site

Appendix B3: **Deferring Selection** of Treatment Components to Remedial Design

Appendix B4: Suggested ROD Language from **1990 OSWER Directive**

Appendix B1: Phased Implementation of Ground-Water Remedy

<u>**Site Conditions**</u> **:**

At **hypothetical Site 1** (an LNAPL site) surficial soils and the underlying ground water in Aquifer C are contaminated with volatile organic compounds (VOCs). At this site, Aquifer C is currently used as a source of drinking water, with several wells located on-site and in the estimated path of the contaminant plume.

Early actions were used for exposure prevention and source control. Under Superfund **removal authority** , an alternate water supply was provided to several residences, and leaking drums and heavily contaminated soils were excavated and taken off-site for disposal. A soil vapor extraction system was installed as an **interim remedial action** . No further source control actions are planned. DNAPLs are not likely to be present in the subsurface because most of the contaminants are LNAPLs rather than DNAPLs in pure form. The selected ground-water remedy relies on extraction and treatment for preventing further migration of the contaminant plume and for restoration of Aquifer C.   **The selected remedy will be implemented in two construction phases.**

<u>**ROD Language for Extraction Component of Remedy**</u> **:**

The following, or similar language, should appear in the <u>**Selected Remedy**</u> section of the ROD:

> The **ultimate goal** for the ground-water portion of this remedial action is to restore Aquifer C to its beneficial uses. At this site, Aquifer C is currently used as a source of drinking water. Based on information obtained during the remedial investigation and on a careful analysis of all remedial alternatives, EPA and the State of ___ believe that the selected remedy will achieve this goal.
>
> The **extraction portion of the ground-water remedy** will be implemented in two phases. In **phase one**, a sufficient number of extraction wells will be installed with the **objective of minimizing further migration of the contaminant plume**. It is currently estimated that two to four extraction wells will be required for phase one.[1] After construction of phase one is completed, the extraction system will be carefully monitored on a regular basis and its performance evaluated. **Operation and monitoring of phase one for a period of up to one year may be needed to provide sufficient information to complete the design of phase two.**
>
> In **phase two**, additional extraction wells will be installed with the **objective of restoring Aquifer C** for use as a source of drinking water, in addition to maintaining the remedial objectives for phase one. Restoration is defined as attainment of required cleanup levels in the aquifer, over the entire contaminant plume. Cleanup levels for each ground-water contaminant of concern are specified in Table __ of the ROD. Current estimates indicate that an additional two to four extraction wells may be required to attain these cleanup levels within a timeframe of approximately 20 years.[1] However, **monitoring and evaluation of the performance of phase one will be used to determine the actual number and placement of wells for phase two**.

Appendix B1: Phased Implementation of Ground-Water Remedy   (continued)

*The selected remedy will include ground-water extraction for an estimated period of 20 years, during which the system's performance will be carefully monitored, in accordance with the monitoring plan defined in Section ___ of the ROD, and adjusted as warranted by the performance data collected during operation. **Refinement** of the extraction system may be required, if EPA determines that such measures will be necessary in order to restore Aquifer C in a reasonable timeframe, or to significantly reduce the timeframe or long-term cost of attaining this objective. **Refinement of the extraction system may include any or all of the following:***

> 1) *Adjusting the rate of extraction from some or all wells;*
>
> 2) *Discontinuing pumping at individual wells where cleanup goals have been attained;*
>
> 3) *Pulsed pumping of some or all extraction wells to eliminate flow stagnation areas, allow sorbed contaminants to partition into ground water, or otherwise facilitate recovery of contaminants from the aquifer; and*
>
> 4) *Installing up to two additional ground-water extraction wells to facilitate or accelerate cleanup of the contaminant plume.[1]*

*It is possible that performance evaluations of the ground-water extraction system - after completion of phase one, during implementation or operation of phase two, or after subsequent refinement measures - will indicate that restoration of Aquifer C is technically impracticable from an engineering perspective. **If such a determination is made by EPA, the ultimate remediation goal and/or the selected remedy may be reevaluated.**[2]*

NOTES:

1.   Although not required in a ROD, the **estimated number of wells** is included in this example for the following reasons, to:

- Provide a **basis for estimating the cost** of the selected remedy, including upper and lower costs for phase one, phase two and the potential refinement measures;

- Provide some **specificity regarding how the extraction component of the remedy will be used in the overall remediation strategy** , because changes in the extraction system directly influence the time period required to attain the remedial objectives for this site; and to

- Provide some **bounds for the scope, performance and cost of the selected remedy**, which will assist in determining whether future, post-ROD remedy modifications require an Explanation of Significant Differences (see Section 2.4 of this guidance).

2.   Reevaluation of the ultimate remediation goal and/or the selected remedy would generally require an ESD or ROD amendment.

Appendix B2: Phased Implementation of Extraction Component of Remedy at a DNAPL Site

<u>Site Conditions</u>:

At **hypothetical Site 2** (a DNAPL site), ground water in Aquifer A is contaminated with volatile and semivolatile organic contaminants (no metals as contaminants of concern). DNAPLs have also been observed in this aquifer. At this site, Aquifer A is not currently used as source of drinking water, but several wells are located off-site in the estimated path of the contaminant plume.

The selected remedy includes extraction and treatment for hydraulic containment of the likely **DNAPL-zone** (see Appendix A1 of this guidance) and for restoration of the aquifer outside the DNAPL-zone. Reinjection of a portion of the treated ground water will be used to enhance recovery of contaminants from the aquifer. It has been determined that aquifer restoration within the DNAPL-zone is technically impracticable from an engineering perspective, as explained in the <u>**Statutory Determinations**</u> section of the ROD. **The remedy will be implemented in two construction phases.**

<u>ROD Language for Extraction Component of Remedy</u>:

The following, or similar language, should appear in the <u>**Selected Remedy**</u> section of the ROD:

> The **ultimate goal** for the ground-water portion of this remedial action is to restore the maximum areal extent of Aquifer A to its beneficial uses. At this site Aquifer A is potentially useable as a source of drinking water and is currently used off-site for this purpose. Based on information obtained during the remedial investigation and on a careful analysis of all remedial alternatives, EPA believes that the selected remedy will achieve this goal.
>
> The **extraction portion of the ground-water remedy** will be implemented in two phases. In **phase one**, a sufficient number of extraction wells will be installed to achieve **two remedial objectives for Aquifer A**: 1) minimizing further migration of contaminants from suspected subsurface DNAPL areas to the surrounding ground water; and 2) minimizing further migration of the leading edge of the contaminant plume. It is currently estimated that three to five extraction wells will be required for phase one.[1] After construction of phase one is completed, the extraction system will be carefully monitored on a regular basis and its performance evaluated. This evaluation may provide further information concerning the extent of the DNAPL-zone. **Operation and monitoring of phase one for a period of up to two years may be needed to provide sufficient information to complete the design of phase two.**
>
> In **phase two**, additional extraction wells will be installed with the objective of **restoring the maximum areal extent of Aquifer A** for use as a source of drinking water, in addition to maintaining phase one objectives. Reinjection wells and related pumping equipment for flushing a portion of the treated ground water through the aquifer (water flooding) will also be installed in order to enhance the recovery of contaminants. Restoration is defined as attainment of required cleanup levels in the aquifer, over the portion of the contaminant plume outside the DNAPL-zone. Cleanup levels for each ground-water contaminant of concern are specified in Table __ ; although cleanup level ARARs within the DNAPL-zone have been waived by EPA due technical impracticability from an engineering perspective, as discussed in Section __ of the ROD. Current estimates indicate that these cleanup levels can be attained in the portion of Aquifer A outside the DNAPL-zone within a timeframe of approximately 25 years.

Appendix B2: Phased Implementation of Extraction Component of Remedy at a DNAPL Site (continued)

Current estimates also indicate that an additional two to six extraction wells and two to four reinjection wells may be required for phase two.[1] ***However, monitoring and evaluation of the performance of phase one will be used to determine the actual number and placement of wells for phase two.***

*The selected remedy will include ground-water extraction for an **estimated period of 25 years**, during which the system's performance will be carefully monitored, in accordance with the monitoring plan defined in Section ___ of the ROD, and adjusted as warranted by the performance data collected during operation.* ***Refinement*** *of the extraction system may be required, if EPA determines that such measures will be necessary in order to restore the maximum areal extent of Aquifer A in a reasonable timeframe, or to significantly reduce the timeframe or long-term cost of attaining this objective.* ***Refinement of the extraction system may include any or all of the following:***

1) *Adjusting the rate of extraction from some or all wells;*

2) *Discontinuing pumping at individual wells where cleanup goals have been attained;*

3) *Pulsed pumping of some or all extraction wells to eliminate flow stagnation areas, allow sorbed contaminants to partition into ground water, or otherwise facilitate recovery of contaminants from the aquifer;*

4) *Installing up to two additional ground-water extraction wells to facilitate or accelerate cleanup of the contaminant plume; and[1]*

5) *Installing up to two additional reinjection wells.[1]*

It is possible that performance evaluations of the ground-water extraction system - after completion of phase one, during implementation or operation of phase two, or after subsequent refinement measures - will indicate that restoration of portions or all of Aquifer A is technically impracticable from an engineering perspective. ***If such a determination is made by EPA, the ultimate remediation goal and/or the selected remedy may be reevaluated.[2]***

NOTES:

1. The reasons for including the **estimated number of wells** in this example are discussed in the Notes section of the previous example, Appendix B2.

2. Reevaluation of the ultimate remediation goal and/or the selected remedy would generally require an ESD or ROD amendment.

Appendix B3: Deferring Selection of Treatment Components to Remedial Design

Site Conditions:

Hypothetical Site 2 is the same site used in the previous example, Appendix B2. Most of the treated ground water will be discharged to the nearby Muddy River, although a portion (20 to 30 percent) will be reinjected to Aquifer A to enhance contaminant recovery. Contaminant-specific and other water quality requirements for discharge to the Muddy River were specified by the state and are listed in Table ___ of the ROD. Other specifications for the treatment system are also listed in the ROD, which include filtering of suspended mineral solids to minimize clogging of reinjection wells; and treatment of vapor phase organic contaminants from air stripping or other processes, as requested by the local community.

ROD Language for Treatment Component of Remedy:

> The **ex-situ treatment component of the ground-water** remedy will utilize presumptive technologies identified in Directive 9283.1-12 from EPA's Office of Solid Waste and Emergency Response (OSWER), included as Attachment __ of the ROD. Since contaminants of concern include volatile and semivolatile organic compounds, **one or more of the presumptive technologies** - air stripping, granular activated carbon (GAC), chemical/UV oxidation and aerobic biological reactors - will be used for treating aqueous contaminants in the extracted ground water. Other technologies will also be needed in the treatment system for removal of suspended mineral solids and treatment of vapor phase contaminants. **The actual technologies and sequence of technologies used for the treatment system will be determined during remedial design.** Final selection of these technologies will be based on additional site information to be collected during the remedial design. (See Section 3.4 and Appendix C3 of OSWER Directive 9283.1-12 for a discussion of site information needed for selection and design of the ex-situ treatment system.) Based on this additional information and sound engineering practice the treatment system shall be designed to:
>
> - Attain the chemical-specific discharge requirements and other performance criteria specified in Table __ and Section __ of the ROD; and
>
> - Treat, or be easily modified to treat, the expected flow increase from phase one to phase two of the extraction system.
>
> Other design factors shall include:
>
> - Maximizing long-term effectiveness,
>
> - Maximizing long-term reliability (i.e., minimize the likelihood of process upsets), and
>
> - Minimizing long-term operating costs.
>
> Additional information concerning presumptive technologies for the ex-situ treatment component of the remedy is provided in OSWER Directive 9283.1-12. Descriptions of each of the presumptive technologies are presented in Appendices D1 through D8, and advantages and limitations of each of these technologies are listed in Appendix C4 of this directive.

Appendix B3: Deferring Selection of Treatment Components to Remedial Design   (continued)

> ***For the purpose of estimating the approximate cost of the treatment component*** *of the selected remedy, the following treatment sequence is assumed for* ***aqueous contaminants****: flow equalization tanks, a gravity oil-water separator, an air stripper, followed by GAC units. GAC will also be used to treat* ***vapor phase contaminants*** *from the air stripper. The GAC units will be thermally reactivated at an off-site facility. Separated DNAPL compounds will be recycled if possible, but since the actual composition of the recovered liquids is unknown, costs for incineration at an off-site facility were used for the cost estimate.*

Appendix B4: Suggested ROD Language from 1990 OSWER Directive

Recommended language for the Selected Remedy section of the ROD was given in OSWER Directive 9283.1-03, entitled "Suggested ROD Language for Various Ground-Water Remediation Options," dated October 10, 1990. For the RODs in which the final remedy without a contingency is selected, this Directive recommended that "the following type of language should appear in the **Selected Remedy** section of the ROD:"

> *The goal of this remedial action is to restore ground water to its beneficial use, which is, at this site, (specify whether this is a potential or actual drinking water source, or is used for non-domestic purposes). Based on information obtained during the remedial investigation and on a careful analysis of all remedial alternatives, EPA < (optional) and the State/Commonwealth of _____ > believe that the selected remedy will achieve this goal. It may become apparent, during implementation or operation of the ground-water extraction system and its modifications, that contaminant levels have ceased to decline and are remaining constant at levels higher than the remediation goal over some portion of the contaminated plume. In such a case, the system performance standards and/or the remedy may be reevaluated.*

> *The selected remedy will include ground-water extraction for an estimated period of _____ years, during which the system's performance will be carefully monitored on a regular basis and adjusted as warranted by the performance data collected during operation. Modifications may include any or all of the following:*

> > *a) at individual wells where cleanup goals have been attained, pumping may be discontinued;*

> > *b) alternating pumping at wells to eliminate stagnation points;*

> > *c) pulse pumping to allow aquifer equilibration and to allow adsorbed contaminants to partition into ground water; and*

> > *d) installation of additional extraction wells to facilitate or accelerate cleanup of the contaminant plume.*

> *To ensure that cleanup goals continue to be maintained, the aquifer will be monitored at those wells where pumping has ceased on an occurrence of every _____ years following discontinuation of ground-water extraction.*

APPENDIX C

Ex-Situ Treatment Technologies for Ground Water

Appendix C1: Ex-Situ Technologies Considered in Sample of 25 Sites

Technologies that were **considered** for treatment of extracted ground in the sample of 25 sites reviewed in detail (EPA, 1996b) are listed below. These technologies were either considered in the feasibility study (FS), or considered and/or selected in the record of decision (ROD) or remedial design. The technologies are listed according to overall process type, and by design style within each type. Those technologies identified as **presumptive technologies** are also indicated. For further information on how presumptive technologies were identified, refer to Section 3.2 of this guidance and EPA, 1996b.

For Treatment of **Organic** Contaminants:

Presumptive Technologies:

Air stripping:
- Packed tower
    - Ambient temperature
    - Higher temperature
- Aeration methods
    - Ambient temperature
    - Higher temperature
- Cascade falls

Granular activated carbon (GAC)

Chemical/UV oxidation:
- Chemical oxidation alone
    - Ozone
    - Hydrogen peroxide
    - Chlorine compounds
    - Potassium permanganate
- Chemical with UV oxidation
    - Ozone
    - Hydrogen peroxide
- UV oxidation alone (photolysis)
- Alkaline chlorination (**for cyanide**)
- Unspecified oxidation methods

Aerobic biological reactors:
- Attached growth
    - Trickling filter
    - Rotating biological contactors
    - Fixed bed
- Suspended growth
    - Activated sludge
    - Sequencing batch reactors
    - Aeration ponds/lagoons
    - Unspecified suspended growth
- Unspecified aerobic reactors

For Treatment of **Metals**:

Chemical precipitation:
- Hydroxide precipitants
    - Sodium hydroxide
    - Lime
    - With prior chemical reduction
- Sulfide precipitants
    - Sulfur dioxide
    - Sodium sulfide
    - Sodium bisulfide/bisulfites
    - With prior chemical reduction
    - Unspecified sulfide precipitant
- Other precipitation methods
    - Ferrous sulfate
    - Potassium permanganate
    - Activated consumable element
    - Unspecified chemical precipitation

Ion exchange/adsorption:
- Fixed bed
    - Impregnated/synthetic resin
    - Activated alumina
- Electrodialysis
- Unspecified ion exchange

Electrochemical methods:
- Electrochemical reduction
- Magnetically activated

Aeration of Background Metals:
- Aeration basin
- Cascade aeration
- Other aeration methods

Appendix C1: Ex-Situ Technologies Considered in Sample of 25 Sites (continued)

For Treatment of **Organic** Contaminants:

Other Technologies Considered:

Chemical treatment:
- Hydrolysis
- Catalytic dehydrochlorination
- Catalytic dechlorination
- Chlorinolysis

Thermal Destruction:
- Incineration
- Calcination
- Wet air oxidation
- Supercritical water oxidation
- Microwave discharge/plasma

High temperature separation:
- Steam stripping
- Distillation

Membrane filtration:
- Reverse osmosis
- Ultrafiltration

Anaerobic biological treatment:
- Anaerobic biological reactor
- Enzymatic degradation

Liquid-liquid extraction:
- Solvent extraction
- Liquid carbon dioxide extraction

Evaporation:
- Evaporation basin

Land treatment:
- Surface spreading
- Spray irrigation

For Treatment of **Metals**:

Granular activated carbon (for metals)

Reverse Osmosis

Biological treatment of metals

Appendix C2: Other Components Needed for Treatment Trains [1]

Solid or Liquid Separation Technologies	Effluent Polishing Technologies[2]	Vapor Phase Treatment Technologies[3]
● Oil/grease separation[4]	● Activated carbon	● Activated carbon
● Filtration[5]	● Ion exchange	● Resin adsorption
● Coagulation[5] (or flocculation)	● Neutralization	● Catalytic oxidation
● Clarification[5] (or sedimentation)		● Thermal incineration
		● Acid gas scrubbing
		● Condensation

General Sequence of Unit Processes Used in Aqueous Treatment Trains

Sequence	Unit Treatment Process	Treatment Stage
Begin	Equalize inflow	Pretreatment
	Separate solid particles	Pretreatment
	Separate oil/grease (NAPLs)	Pretreatment
	Remove metals	Treatment
	Remove volatile organics	Treatment
	Remove other organics	Treatment
	Polish organics[2]	Post-treatment
	Polish metals	Post-treatment
End	Adjust pH, if required	Post-treatment

NOTES:

[1]   In addition to the presumptive technologies listed in the guidance, other treatment components are needed either prior to (pretreatment) or subsequent to (post-treatment) the presumptive technologies. This listing is not intended to be presumptive. Not listed are technologies that may be required for treatment residuals, such as spent carbon.

[2]   Effluent polishing technologies are those used for the final stage of treatment prior to discharge, and can include pH adjustment (neutralization) as well as additional removal of aqueous constituents.

[3]   Vapor phase contaminants released during water treatment may need to be contained and treated. This includes organic contaminants volatilized during air stripping, from biological treatment, or other gases released from chemical oxidation, reduction or biologic processes (e.g., hydrochloric acid, hydrogen sulfide, methane, etc.).

[4]   Methods for separation of oil and/or grease from water include, but are not limited to, gravity separation and dissolved air floatation. These methods can be used to remove NAPLs from the extracted ground water.

[5]   These technologies can be used to remove solid particles at the beginning of the treatment train or for removal of other solids resulting from chemical precipitation, chemical/UV oxidation or biological treatment.

Appendix C3: Information Needed for Selection of Technologies and Design of Treatment Train

Information Needed	Purpose of Information
1. Total extraction flow rate:	**Inflow** to the treatment system is the total flow from all extraction wells. Since this flow must also be discharged, large flows may determine the availability of some discharge options. Flow rate and concentration determines the mass loading (mass per unit water volume) of each contaminant entering the treatment system. The mass loading determines the dimensions and capacities of treatment vessels, and whether continuous flow or batch design are used for each treatment unit. Flow is also a factor for selecting among the presumptive treatment technologies because some are less cost effective for high or low flows.
• Total extracted flow	
• Flow variability	
• Uncertainty of estimate	

Variable inflow rates may require use of flow equalization tanks, batch instead of continuous flow operation or use of modular treatment units that can be added or subtracted from the treatment train. Some technologies can handle variable flow more easily than others. Variable extraction rates may result from short-term operational changes, seasonal changes or phased well installation.

Uncertainty in the flow estimate can result from natural variability of aquifer properties over the site, and from the method used to measure these properties. Since flow is a critical design parameter, additional characterization may be needed to reduce the level of uncertainty. **Estimates of the total extraction rate should be based on pumping type aquifer tests, since this method provides a much better estimate of average aquifer properties than other methods.**

Appendix C3: Information Needed for Selection of Technologies and Design of Treatment Train (continued)

Information Needed	Purpose of Information
2. Discharge options and effluent requirements:	Options for discharge of treated ground water could include: discharge to surface waters; discharge to a drinking water system; reuse or recycling for other purposes (e.g., industrial processes); infiltration or reinjection to shallow subsurface or reinjection to the same aquifer; or discharge to POTW. Target effluent concentration levels for both contaminants and naturally occurring constituents may be markedly different for each discharge option.
• Options available	
• Target effluent concentrations, each option	
- Contaminants	
- Contaminant degradation products	Effluent requirements could include those for chemicals added during treatment, contaminant degradation products, naturally occurring constituents (e.g., arsenic), and water quality parameters (e.g., suspended solids) in addition to maximum concentration levels for chemicals of concern. These requirements will determine the overall level of treatment needed, which in turn determines the type of components needed in the treatment train and is a critical factor in selecting appropriate treatment technologies.
- Treatment additives	
- Natural constituents	
- Water quality parameters	
• Other requirements, each option	
- Regulatory	Each discharge option may have different water quality requirements for the treated effluent, from both a **regulatory** and **operational** standpoint. For example, reinjection to the subsurface must meet substantive federal and/or state requirements for underground injection (regulatory) as well as minimize chemical and biological clogging of injection wells or infiltration lines (operational). Use of the best available technology (BAT) could also be a regulatory requirement. The **affected community** may also have concerns or preferences regarding the type of discharge.
- Operational	
• Community concerns or preferences	
	Target effluent concentrations determine the overall removal efficiency the treatment train must attain for each constituent. For example, if the target effluent level is 10 mg/L and the inflow concentration is 1000 mg/L, then the treatment train must attain an overall removal efficiency of 99.0 percent (1000 - 0.99(1000) = 10). The treatment train may need to include more than one type of technology, or multiple units of a single technology, in order to attain the required overall removal efficiency.

Appendix C3: Information Needed for Selection of Technologies and Design of Treatment Train (continued)

Information Needed

Purpose of Information
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3. Water quality of treatment influent:

- Contaminant types and concentrations:

    - Inorganic chemicals

    - Organic chemicals

    - Concentration changes over time

    - Nonaqueous phase liquids (NAPLs)

- Naturally occurring constituents:

    - Major cations (metals) and anions

    - Organic chemicals

    - Radionuclides

Contaminant types and concentrations must be estimated for the total flow entering the treatment system. Since some technologies are more effective in removing certain contaminant types, this is an important technology selection factor. Inflow concentrations are needed to determine the removal efficiency of the treatment train, as discussed above.

The design should consider the potential for inflow concentrations to change over time. Contaminant concentrations usually decrease as remediation progresses. Also, short term increases may occur if a "hot spot" of more highly contaminated ground water is captured by the extraction system. Samples obtained from **pumping type aquifer tests provide better estimates of average contaminant concentrations**, because such samples are obtained from a relatively large aquifer volume.

If present, subsurface **NAPLs** (refer to Appendix A1) may become entrained in the extracted ground water. These immiscible liquids should be removed in a pretreatment step (process used prior to other treatment methods). Also, a specialized extraction system may be needed to remove free-phase NAPLs from the subsurface.

Naturally occurring or non-site related constituents may need to be removed to prevent interference with treatment processes and may be a factor in technology selection. **Metals** such as iron, manganese, and calcium can leave mineral deposits (scaling) on air stripper packing and on activated carbon or other treatment media. If not accounted for, these metals can also cause premature exhaustion of ion exchange capacity and increased consumption of reagents in chemical oxidation or precipitation processes. Iron also promotes biological fouling in air strippers. Heavy metals (e.g., lead, mercury) and cyanides can be toxic to microorganisms in biological reactors. Metals can also form deposits on well screens of extraction or reinjection wells (encrustation) or promote biological fouling (clogging) on well screens.

Appendix C3: Information Needed for Selection of Technologies and Design of Treatment Train (continued)

Information Needed	Purpose of Information
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3. Water quality of influent (continued):

- Other water quality parameters:

    - Indicator parameters

    - Design parameters

Dissolved **organic constituents** (e.g., from decay of organic materials or from landfill leachate) can interfere with adsorption of targeted compounds and can cause premature exhaustion of activated carbon. Metal-organic complexes can interfere with chemical oxidation or precipitation processes.

If present, naturally occurring **radionuclides** can accumulate in treatment media or residuals (e.g., activated carbon or chemical sludges) resulting in potential exposure hazards for personnel and additional transportation and disposal considerations.

Other water quality parameters are used as effluent quality standards, indicator parameters, or design parameters for treatment processes. **Indicator parameters** are used to indicate the presence of other constituents. For example, total dissolved carbon (TDC) is a measure of the relative level of dissolved organic constituents. Gross alpha and gross beta particle activity are relatively simple measurements that indicate the relative abundance of **naturally occurring radionuclides**. Other indicator parameters include: total dissolved solids (TDS), chemical oxygen demand (COD), biological oxygen demand (BOD) and total suspended solids (TSS). Temperature and pH are **design parameters** for most treatment processes.

Also, high levels of total suspended solids (TSS) in extracted ground water may indicate that extraction wells are not properly designed or developed. Most treatment technologies require that suspended solids in excess of certain level be removed during pretreatment, where acceptable levels may differ for each technology.

Appendix C3: Information Needed for Selection of Technologies and Design of Treatment Train (continued)

Information Needed	Purpose of Information

4. Treatability information:

- From technical literature

- Treatability studies

  - Laboratory screening

  - Bench-scale testing

  - Pilot-scale testing

- Modeling predictions

- Projections of effluent quality

Treatability information is needed to select technology types and design styles from among the presumptive technologies; and for selection and design of other components of the treatment train. The particular mix of contaminants and naturally occurring constituents can vary considerably for different sites. Treatability information is available in the **technical literature** for some technologies, including air stripping and granular activated carbon (GAC).

Treatability studies include 1) laboratory screening, 2) bench-scale testing, or 3) pilot-scale testing. These studies may begin with any tier and skip tiers that are not needed (see Section 3.4 of guidance). **Computer models** for predicting treatment performance are available for some technologies.

In general, treatability studies should be performed prior or during the design of any system expected to provide **long-term treatment** of extracted ground water, including systems using presumptive technologies. Treatability studies are needed to accurately predict the effectiveness and cost of a technology for a given site, including construction and operating costs; and the costs of other components of the treatment train. Optimizing the cost effectiveness of the treatment train (i.e., minimizing the total cost per unit volume of water treated) is especially important for systems designed to operate over a long time period.

Treatability studies **may reveal unexpected site conditions**, such as the presence of naturally occurring compounds that interfere with the planned treatment process or that metal contaminants can be effectively removed by removing mineral solids. Such studies are also needed to determine pretreatment requirements, and requirements for treating aqueous, vapor and solid waste streams resulting from a particular treatment process. Treatability studies are needed to determine optimum chemical reagents and reagent quantities for pH adjustment; oxidation, reduction or precipitation of contaminants; and parameters for design of biological and other reactors.

Treatability studies should be performed on samples obtained from **pumping type aquifer tests** instead of from monitoring wells, because such samples are more representative of contaminated ground water that will enter the treatment system. Samples obtained for treatability studies should be obtained after several hours of pumping.

Appendix C4: Advantages and Limitations of Presumptive Treatment Technologies

Technology	Advantages	Limitations
Treatment Technologies for the Removal of Organic Contaminants		
Air Stripping	• Successfully used in hundreds of groundwater applications • Low operating cost relative to other technologies (e.g., energy usage is relatively low). • Operationally simple system requiring a minimum of operator assistance. • Treatability studies often not required for selection or design, but are recommended. • Trained contractors available to implement the technology.	• Contaminants transferred to air, and treatment of air emissions may be required. • Pretreatment for metals removal and pH control may be needed to reduce fouling and corrosion. • Post-treatment (polishing) may be required. • Large surges in influent concentrations can reduce removal efficiency because the efficiency for an individual compound is fixed regardless of influent concentrations. • Air stripping is not as effective for compounds with low Henry's law constants or high solubilities.[b,c] • Cold weather can reduce efficiency.
Granular Activated Carbon	• Successfully used for contaminated ground water at many Superfund and underground storage tank sites. • Operationally simple system requiring a minimum of operator assistance. • Regularly used as a <u>polishing</u> step following other treatment technologies. • Treatability studies generally not required, but are recommended (information is available from carbon vendors). • Trained contractors available to implement the technology. • Generally a cost-effective alternative as single- step treatment for flows less than about 3 gpm.[d]	• Activated carbon is generally too costly for use as a single-step treatment if ground-water chemistry requires high carbon usage rates. • Contaminants are not destroyed but are transferred to another media (i.e., spent carbon must be regenerated or disposed of properly). • Pretreatment for suspended solids removal is often required. • Pretreatment for metals removal and pH control may be needed to reduce fouling and corrosion. • Organic compounds that have low molecular weight and high polarity are not recommended for activated carbon (e.g., acetone). • Naturally occurring organic compounds may exhaust carbon bed rapidly and may interfere with the adsorption of targeted chemicals.

Technology	Advantages	Limitations
Chemical/ UV Oxidation	• Where oxidation is complete, organic contaminants are <u>destroyed</u> and not transferred to other media; minimal residuals generated. • Effective on a wide variety of volatile and semivolatile organics, including chlorinated organics, as well as cyanide and some metals. • Operating costs can be competitive with air stripping and activated carbon.	• Incomplete oxidation will leave original contaminants and possibly toxic oxidation products; activated carbon polishing may be required. • Capital costs may preclude small-scale applications, especially for ozone systems. • Metals may precipitate during oxidation, requiring filtration post-treatment and residuals disposal. • UV light sources are subject to fouling and scaling from solids, iron compounds, carbonates, etc. Pretreatment may be required to remove these substances. • Process must be closely monitored to ensure contaminant destruction and to prevent safety hazards. • Peroxide and other chemical oxidants must be properly stored and handled. • Site-specific treatability studies are necessary (process may require large quantities of oxidizer to destroy target compound(s) if reactive nontarget compounds are present).
Aerobic Biological Reactors	• Organic contaminants <u>degraded</u>, often with minimal cross-media environmental impacts. • Proven effective for many organic compounds. • Some systems (e.g., trickling filters and rotating biological contactors) have minimal energy requirements and generally low capital and operating costs. • Can be designed to require a minimum of operator attention. • Relatively simple, readily available equipment. • Trained contractors available to implement the technology.	• A residual organic sludge is generated that must be disposed of properly. • Some compounds are difficult or impossible to degrade (recalcitrant) or slow to degrade. • Difficulties acclimating microorganisms to contaminants are possible; requires longer startup time than other technologies to achieve effective steady-state performance • Volatile organics may require air emission controls or pretreatment to remove them. • Variations in flow or concentration may require significant operator attention to prevent microorganisms from being killed. • Cold weather can cause operational difficulties. • Treatability studies are needed for selection and design. • Pretreatment may be needed to remove contaminants toxic to the microorganisms, such as heavy metals. • Low organic loading and the potential for supplementary nutrients and food sources must be considered.

Technology	Advantages	Limitations
Treatment Technologies for the Removal of Inorganic Contaminants		
Chemical Precipitation	• Most commonly used method for removing soluble heavy metal ions from contaminated water. • Pretreatment for solids and iron generally not required. <u>Hydroxide Precipitation</u> • Reliable method, chemicals relatively easy to handle, and not costly. <u>Carbonate Precipitation</u> • Reliable method, calcium carbonate easy to handle, and not costly. • Effectively removes a variety of soluble metals. <u>Sulfide Precipitation</u> • Reliable method. • High removal efficiency over a broader pH range. • Relatively insensitive to most chelating agents. • Can remove chromates and dichromates without reducing hexavalent chromium to trivalent form if ferrous ions are present or added.	• A residual sludge is generated that must be treated and/or disposed of properly; metals are not usually easy to recover from sludge. • Up to four times stoichiometric chemical additions may be required, especially for sulfide precipitation (see below). <u>Hydroxide Precipitation</u> • Organics or complexing ions may form chelates/complexes instead of insoluble metal hydroxides. • Optimum pH is different for each metal hydroxide, one pH may not effectively treat all soluble metal ions; successive treatments may be required. • pH must be controlled within a narrow range. • Naturally occurring sulfate in ground water may react with lime to form gypsum, which increases sludge, can clog filters, and can coat pipelines (caustic soda addition can reduce this problem but increases costs and dissolved solids [sodium salts] that must be removed from treated ground water). <u>Carbonate Precipitation</u> • Calcium carbonate is not effective for ground water with high alkaline content. • Pretreatment to remove organic, chelating, or oil and grease contaminants may be required. <u>Sulfide Precipitation (Soluble Sulfide)</u> • Excess sulfide ions that are not precipitated remain in solution. They may be removed by using aeration to convert them from ionic to oxide form (sulfate). • pH control between 8 and 9.5 is required to avoid release of hydrogen sulfide gas. • Cost is high compared to hydroxide and carbonate precipitation <u>Sulfide Precipitation (Insoluble Sulfides)</u> • Ferrous sulfide is used in amounts greater than that required by stoichiometric considerations. • Produces more sludge than soluble sulfide or hydroxide processes.

Technology	Advantages	Limitations
Treatment Technologies for the Removal of Inorganic Contaminants (continued):		
Ion Exchange/ Adsorption	• High removal efficiencies for heavy metals. • Suitable for use as a <u>polishing</u> step after other technologies. • Technology is reasonably well understood. • On-site backflushing of exchange media allows immediate reuse.	• Resins are usually costly and may not be cost-effective for large treatment loadings. • Generates large volume of backflush solution (approximately 2.5 to 5% of the original ground-water flow rate) that is concentrated in the metals removed and requires treatment or disposal. • Requires bench-scale testing to determine operational requirements and suitability of prospective resins. • Beds can be fouled by particulate matter, oxidizing agents, oils, greases, biological growths, and intra-bed precipitates; therefore, pretreatment may be needed. • Resins may be irreversibly harmed by aromatics and certain other organic compounds; and by iron, manganese, and copper if enough dissolved oxygen is present. Pretreatment may be needed. • Spent resins require treatment before disposal.
Electro-chemical Methods	• High removal efficiencies for certain heavy metals. • Can treat both metals and cyanide simultaneously. • Technology is reasonably well understood. • Requires little floor space due to short residence time for hexavalent chromium reduction. • Requires minimal operator attention. • Low operating costs compared to chemical reduction or precipitation. • Requires no chemical addition.	• Particulate matter, oxidizing agents, oils, greases, biological growths may reduce process efficiency; therefore, pretreatment may be needed. • Hexavalent chromium reduction generates a heavy metal precipitate that must be removed from solution in a subsequent clarification or settling process. • A heavy metal sludge residual may be generated that may require treatment (dewatering and/or fixation) and that will require disposal. • A spent acid rinse solution may be generated that requires treatment or disposal. • Electrodes must be replaced occasionally.

NOTES:

[a] U.S. Environmental Protection Agency. 1991. Engineering Bulletin: *Air Stripping of Aqueous Solutions*. EPA/540/2-91/022. 8 pp.

[b] B. Lamarre. 1993. Selecting an air stripper (what to consider!) *The National Environmental Journal*: 26-29.

[c] G. M. Long. 1993. Clean up hydrocarbon contamination effectively. *Chemical Engineering Progress*: 58-66.

APPENDIX D

Descriptions of Presumptive Treatment Technologies

Appendix D1: Air Stripping

Air stripping uses volatilization to transfer contaminants from ground water to air. In general, water is contacted with an air stream to volatilize dissolved contaminants into the air stream. Stripping of a specific chemical depends on the equilibrium vapor pressure of that chemical as expressed by its Henry's law constant.

Applicability

Air stripping is *applicable* to most of the volatile organic compounds (VOCs) as well as volatile inorganics such as ammonia and hydrogen sulfide. VOCs with high solubility in water (e.g., acetone) are more difficult to air strip. Air stripping is *potentially applicable* to certain halogenated semi-volatile organic compounds (SVOCs). It is *not applicable* to nonhalogenated SVOCs; heavy organics such as PCBs, dioxins/furans and pesticides; or inorganic metal compounds (U.S. EPA, 1991).

Air stripping is most effective for contaminants with a dimensionless (molar volume) Henry's law constant greater than 0.01 (or 2.4×10^{-4} atm-m^3/gmol at 25° C). (Henry's law constants are available in U.S. EPA [1990]). Removal efficiencies greater than 99 percent are difficult to achieve for certain compounds. In general, other treatment technologies will be required for such chemicals when ground-water concentrations are high (e.g., above 10,000 ppm or 1 percent).

Contaminant Fate

Contaminants are not destroyed by air stripping but are physically separated from contaminated ground water and transferred to air. Depending on the level of contaminants in the air discharge, the contaminated air stream may need further treatment. Additional polishing treatment of the aqueous effluent also may be necessary, depending on discharge requirements.

Design

Air strippers are designed for a specific target chemical (either the predominant contaminant or the most difficult-to-strip contaminant) with a desired target removal efficiency. The air stripping process is well understood and the technology is well developed. Air stripping has an extensive track record in a variety of applications.

The most frequently used configuration is a packed tower equipped with an air blower. The ground water is fed into the top of the stripper and the air is introduced at the bottom, creating a countercurrent gas-liquid contact. Random plastic packing is frequently used to improve gas-liquid contact. Structured packing and steel packing may also be used. Packed-tower air stripper design involves specification of stripper column diameter and packing height for a specified ground-water flow rate and air-to-water ratio. Shallow-tray aeration devices provide an alternative gas-liquid contacting system that provides a more compact, lower profile system that is less subject to fouling.

Alternative Techniques/Enhanced Methods

- For high flow rates (over 1,000 gpm), cooling towers (large structures with cascading water primarily used to cool water using countercurrent ambient air flow) may provide a cost-effective alternative to conventional packed towers.

- Shallow tray air strippers or diffused tank aeration units are less susceptible to fouling problems than packed towers and may be preferable where the water to be treated contains high concentrations of certain inorganics (e.g., iron).

Alternative Techniques/Enhanced Methods (continued)

- Because the efficiency of air stripping increases at higher temperatures, increasing the influent ground-water temperature (typically about 55° F) using a heat exchanger can increase the stripper's removal efficiency, especially for less volatile contaminants.

- Steam stripping methods, which use steam rather than air as the stripping medium, can be used to remove highly soluble contaminants and SVOCs not usually amenable to air stripping. However, operation costs for steam stripping can be two to three times greater than air stripping, depending on the cost of steam. In this guidance, these methods are not considered a type of air stripping and are not identified as a presumptive technology for ex-situ treatment of ground water.

Pre/Post-treatment

- Pretreatment to remove iron and other metals and to control hardness may be necessary to reduce fouling and mineral deposition in packed tower air strippers.

- Granular activated carbon is sometimes used to polish the treated water from an air stripper to further reduce organic contaminant levels and meet discharge requirements.

- Contaminants in the air discharge may be reduced by activated carbon adsorption, catalytic oxidation, or incineration to meet air emission requirements.

Selected References

Lamarre, B. 1993. Selecting an air stripper (what to consider!). The National Environmental Journal: 26-29.

Nyer, E.K. 1985. Groundwater Treatment Technologies. Van Nostrand Reinhold, New York, NY. 187 pp.

Nyer, E.K. 1993. Practical Techniques for Groundwater and Soil Remediation. CRC Press, Inc., Boca Raton, FL. 214 pp.

Okoniewski, B.A. 1992. Remove VOCs from wastewater by air stripping. Chemical Engineering Progress: 89-93.

U.S. EPA Environmental Protection Agency. 1990. Hazardous Waste Treatment, Storage, and Disposal Facilities (TSDF) - Air Emission Models. EPA/450/3-87-026. Office of Air Quality Planning and Standards, Research Triangle Park, NC. Appendix D.

U.S. Environmental Protection Agency. 1991. Engineering Bulletin: Air Stripping of Aqueous Solutions. EPA/540/2-91/022. Office of Research and Development, Cincinnati, OH. 9 pp.

Appendix D2: Granular Activated Carbon

Activated carbon removes contaminants from ground water by adsorption. The adsorption process takes place in three steps: (1) contaminant migration to the external sorbent surface; (2) diffusion into the sorbent pore structure; and (3) adsorption onto the sorbent surface. The principal form of activated carbon used for ground-water treatment is granular activated carbon (GAC). GAC is an excellent sorbent due to its large surface area, which generally ranges from 500 to 2,000 m^2/g.

Applicability

GAC is *applicable* to a wide variety of contaminants including: halogenated volatile and semivolatile organics, nonhalogenated volatile and semivolatile organics, PCBs, pesticides, dioxins/furans, most organic corrosives, metals, radioactive materials, inorganic cyanides, and certain oxidizers. GAC is *potentially applicable* to certain organic cyanides, and it is *not applicable* to asbestos, inorganic corrosives, and reducers (U.S. EPA, 1991). GAC is sometimes used alone for ground-water treatment. However, GAC is typically used for polishing aqueous effluents or controlling air emissions from other treatment technologies.

The adsorption capacity of activated carbon varies for specific organic compounds and for different types of GAC (based on the origin of coal and the percent binder used in the manufacture of the GAC). Contaminant-specific adsorption isotherms for a given type of GAC are generally available from the carbon manufacturer.

Contaminant Fate

Contaminants are not destroyed by carbon adsorption, but are physically separated from contaminated water and transferred to carbon. After exhaustion, the spent carbon may be reactivated, regenerated, incinerated, or disposed of. Thermal reactivation and incineration destroy most or all adsorbed organic contaminants. Steam or hot gas regeneration is not appropriate for spent GAC from treatment of contaminated ground water but can be used for spent GAC from air emission control devices. GAC used for metals sorption may require disposal. If disposed of, spent GAC may have to be managed as a hazardous waste.

Design

Activated carbon is a well-developed, widely used technology with many successful ground-water treatment applications, especially for secondary polishing of effluents from other treatment technologies. Contaminated ground water is contacted with a fixed GAC bed in a vessel. Flow direction is generally vertically downward, although an upward flow configuration is also possible. Fixed-bed configurations are also used for air emission control.

Adsorber design involves determining total carbon requirements and the number and dimensions of vessels needed to house the carbon. The amount of carbon required for a given application depends on the loading of adsorbable constituents in ground water (or contaminated air stream), the carbon's adsorption capacity for these constituents, and the carbon reactivation (or regeneration) frequency. Depending on the ground-water suspended solids content, it may be necessary to periodically backwash down flow carbon beds to relieve pressure drop associated with solids accumulation.

Alternative Techniques/Enhanced Methods

- Staged bed (multiple beds operated in series) and pulsed bed (carbon beds operated with nearly continuous "pulsed" addition of fresh carbon and withdrawal of spent carbon) designs can be used if higher removal efficiencies are required.

Alternative Techniques/Enhanced Methods (continued)

- Because the adsorption capacity of GAC is much higher for gas phase treatment than for liquid phase treatment, it is often more economical to use an air stripper followed by gas phase GAC to treat the air stripper exhaust than to use GAC alone for ground-water treatment.

- **GAC is not identified as a presumptive technology for removal of metals dissolved extracted ground water. Spent carbon used for metals removal can be difficult to regenerate and may require treatment and/or disposal as a hazardous waste.** Although GAC can remove low concentrations of certain metals, it has not been widely used for this purpose (U.S. EPA, 1991).

Pre/Post-treatment

- Pretreatment may be required to remove natural organic matter, such as fulvic and humic acids, that may interfere with the adsorption of the target contaminants or rapidly exhaust the GAC.

- Naturally occurring **radionuclides**, if present in ground water, can accumulate in the GAC during treatment, **which could result in potential exposure hazards for operating personnel and the spent carbon may require treatment and/or disposal as hazardous waste**.

- Thermal reactivation, using heat alone or steam, is typically used as a post-treatment method for the spent carbon. The carbon is reactivated in a high-temperature reactor under reducing conditions. Most organic contaminants are thermally degraded during the reactivation process.

Selected References

Long, G.M. 1993. Clean up hydrocarbon contamination effectively. *Chemical Engineering Progress*, 89(5):58-67.

Stover, E.L. 1988. Treatment of herbicides in ground water. *Ground Water Monitoring Review*: 54-59.

Stenzel, M.H. 1993. Remove organics by activated carbon adsorption. *Chemical Engineering Progress*: 36-43.

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Appendix D3: Chemical/UV Oxidation

Chemical oxidation uses chemical oxidizing agents to destroy toxic organic chemicals and cyanide compounds (CN) in ground water. Commonly used oxidizing agents include: ozone, hydrogen peroxide, hypochlorites, chlorine, and chlorine dioxide. Ozone and hydrogen peroxide are generally preferred for removing organics and CN from ground water because chlorine-based oxidants can produce toxic byproducts (e.g., HCl, chlorinated organics). Ultraviolet light (UV) is often used in conjunction with ozone and/or hydrogen peroxide to promote faster and more complete destruction of organic compounds (reaction rates may be increased by factors of 100 to 1,000).

Applicability

Chemical oxidation is *applicable* to both volatile and semivolatile organic compounds and cyanide compounds. Chemical oxidation is *potentially applicable* to PCBs, dioxins/furans, and metals (oxidation can be used to precipitate metals under certain conditions). Chemical oxidation is *not applicable* to asbestos and radioactive materials (U.S. EPA, 1991).

Chemical oxidation generally is effective for concentrations less than 500 µgL, but has been used for certain compounds at concentrations ranging up to several thousand mg/L. UV can enhance the oxidation of compounds that are resistant to chemical oxidation alone (e.g., PCBs). Iron or copper catalysts may be required for efficient destruction of certain organic compounds (e.g., phenols).

Contaminant Fate

Complete oxidation decomposes hydrocarbons into carbon dioxide and water, although chlorinated organic compounds also yield chloride ions. CN is oxidized to ammonia and bicarbonate by hydrogen peroxide in an alkaline environment. If oxidation is incomplete, toxic constituents may remain, or intermediate degradation products can be formed that may be toxic. These toxic substances may be removed using GAC as a secondary or polishing treatment step.

Design

Chemical oxidation is a proven and effective technology that is carried out in either batch or continuous reactors. Oxidants are generally added to contaminated ground water in a mixing tank prior to introduction into the reaction vessel (reactor). The use of ozone as the oxidizing agent requires an onsite ozone generator and an ozone decomposition unit or other ozone emission control device. The use of hydrogen peroxide as the oxidizing agent requires storage tanks and special handling protocols to ensure operator safety. The use of chlorine as the oxidizing agent may produce HCl gas. If HCl is produced, an acid gas removal system may be necessary.

UV lamps, if used, are typically enclosed in quartz tubes submerged inside the reaction vessel. The tubes are subject to fouling or scaling from compounds such as iron oxide or calcium carbonate and from biological flocs from microorganisms in ground water. If fouling occurs, oxidation rates are drastically reduced.

Site-specific treatability studies are generally recommended for chemical oxidation systems. Extensive pretreatment may be required to condition ground water for effective oxidation. If UV lamps are used, the studies must evaluate the potential for fouling or scaling of the quartz tubes at the ground-water composition, oxidant concentration, and UV intensity conditions anticipated for long-term system operation. If fouling or scaling is likely, pretreatment and/or physical methods for keeping the tubes clean (e.g., wipers) may be required. If metals are to be removed by oxidation, solids should be removed by clarification or filtration prior to UV oxidation. Provisions for removing precipitated metal sludges also may be necessary.

Alternative Techniques/Enhanced Methods

● UV radiation can be used in combination with a chemical oxidizing agent to increase the effectiveness of oxidation, especially for difficult-to-oxidize compounds.

● Metal catalysts, such as iron or copper, can be used in combination with a chemical oxidizing agent to increase the effectiveness of oxidation for certain types of compounds.

● Hydrodynamic cavitation is an innovative technology recently demonstrated under EPA's SITE program that uses forced cavitation of gas to enhance destruction of organics during UV oxidation processes.

Pre/Post-treatment

● Pretreatment may be necessary to remove solids, microorganisms, calcium carbonate, iron oxides, and/or other metals that can interfere with the oxidation process or UV transmission. A pretreatment sequence of precipitation, flocculation, clarification, and/or filtration steps may be necessary.

● Post-treatment of the aqueous effluent with GAC may be necessary if destruction is not complete or if toxic byproducts are formed during oxidation.

● If toxic metals precipitate during the oxidation process, treatment and/or proper disposal of the resulting sludge may be required.

Selected References

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Appendix D4: Aerobic Biological Reactors

Biological reactors use microorganisms to degrade organic contaminants in ground water in ex situ reactors. There are two basic types of ex situ biological treatment processes: aerobic reactors and anaerobic reactors. Aerobic reactors use oxygen to promote biodegradation and are widely used. Anaerobic reactors degrade organics in the absence of oxygen. This guidance focuses on aerobic biological treatment because anaerobic treatment processes are not widely used for ground-water treatment.

Applicability

Aerobic biological reactors are *applicable* to a wide variety of halogenated and nonhalogenated volatile and semivolatile organics. Aerobic biological reactors are *potentially applicable* to heavy organics, such as PCBs and certain pesticides, and organic and inorganic cyanides, but are generally not as effective for such recalcitrant compounds. Aerobic processes are *not applicable* to metals, asbestos, radioactive materials, or corrosive or reactive chemicals (U.S. EPA, 1992).

Contaminant Fate

Organic compounds are decomposed to carbon dioxide and water (aerobic processes) or to methane and carbon dioxide (anaerobic processes). Volatile organics are also removed by volatilization as a competing mechanism. Microbial growth produces an excess organic sludge (biomass) that must be disposed of properly. This sludge may concentrate metals and recalcitrant organic compounds that are resistant to degradation. Biodegradation may produce decomposition byproducts that are emitted to the air or dissolved in the effluent, and these decomposition byproducts may require additional treatment.

Design

Ex situ biological treatment of ground water is conducted in bioreactors. The primary factors influencing bioreactor design are the microbial organic utilization rates and the peak organic loading rate (i.e., flow rate times organic concentration). Treatability tests are necessary to determine these and other design parameters. Under most circumstances, bioreactors require a significant startup time to acclimate the microorganisms to the specific contaminants being treated before the bioreactor will operate at optimal degradation rates. There are two general types of bioreactor design:

- In **suspended growth** reactors, microbes are kept suspended in water using mechanical aerators or diffused air systems. These aeration systems also keep the solution well mixed, improving contact between microbes and dissolved contaminants and supplying oxygen to the system. Activated sludge systems are the most common suspended growth bioreactors. Other examples include aerated ponds or lagoons, stabilization ponds (using both algae and bacteria), and sequencing batch reactors.

- In **attached growth** reactors, biomass is attached to a solid substrate, such as sand, rock, plastic, activated carbon, or resin. Reactor design is dependent upon the surface area of substrate media available for biomass growth. Examples include trickling filter, rotating biological contactor, fluidized bed, fixed bed, and roughing filter designs.

Alternative Techniques/Enhanced Methods

- Direct addition of powdered activated carbon (PAC) into suspended growth bioreactors can both improve removal efficiency and reduce the likelihood of process upsets by buffering the concentrations of toxic compounds at levels amenable to biodegradation.

Appendix D4: Aerobic Biological Reactors (continued)

Alternative Techniques/Enhanced Methods (continued)

- Microbial augmentation (the addition of specially cultured microorganisms) may be used to increase the system's removal efficiency for certain difficult-to-degrade contaminants.

- Anaerobic reactors (digesters) may be preferred for the treatment of certain ground-water contaminants (e.g., certain chlorinated organics) that are difficult to degrade aerobically. **However, anaerobic reactors have not been identified as a presumptive technology for the following reasons**: 1) anaerobic processes have not been widely used for ground-water treatment; 2) reaction rates are slower than for aerobic processes, which result in longer startup times (for acclimation) and longer treatment times; and 3) such reactors have a greater sensitivity to process upsets, especially where flow and contaminant concentrations vary over time. These factors generally result in higher operation and maintenance requirements and costs, and lower performance efficiencies than for aerobic processes in ground-water applications.

Pre/Post-treatment

- Chemical precipitation (for metals) or other pretreatment (e.g., PAC addition for organics) may be required to reduce (or buffer) concentrations of compounds that are toxic to microorganisms.

- Carbon adsorption post-treatment may be used to reduce contaminant concentrations in the treated water to meet discharge requirements.

- Because certain aerated bioreactor designs (e.g., mechanically aerated activated sludge systems, aerated ponds and lagoons) present difficulties for direct capture and control of air emissions, an air stripper (with emission controls) may be a cost-effective treatment prior to biodegradation if volatile contaminant emissions need to be controlled. For other bioreactor designs, such as diffused-aeration activated sludge and trickling filter systems, air emissions are more easily captured and can be treated using carbon adsorption, catalytic oxidation, or incineration.

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Appendix D5: Chemical Precipitation

Chemical precipitation chemically converts dissolved metal and/or other inorganic ions in ground water into an insoluble form, or precipitate. Metal ions generally precipitate out as hydroxides, sulfides, or carbonates and are removed as solids through clarification and filtration. In this guidance, chemical precipitation is defined to include chemical precipitation of metals by oxidizing or reducing agents, as well as any pH adjustment (neutralization) and solids removal steps required.

Applicability

Chemical precipitation is *applicable* to dissolved metal and other inorganic ions (such as arsenate and phosphate). Chemical precipitation is *not applicable* to volatile or semivolatile organic compounds (U.S. Navy, 1993).

Contaminant Fate

Dissolved metals are converted to insoluble forms, which are subsequently removed by flocculation, clarification, and/or filtration. The solid residue (chemical sludge) containing the metal contaminant then must be treated and/or disposed of properly.

Design

The process generally takes place at ambient temperatures. Batch reactors are generally favored for lower flowrates (e.g., up to about 50,000 gpd), and usually use two tanks operating in parallel. Each tank can act as a flow equalizer, reactor, and settler, thus eliminating separate equipment for these steps. Continuous systems have a chemical feeder, flash mixer, flocculator, settling unit, filtration system (if used), and control system for feed regulation. Site-specific treatability tests are required to determine the optimum type and dosage of precipitation chemicals, necessary pretreatment steps, and post-treatment requirements for aqueous effluent and sludge residuals.

There are three types of precipitation chemicals:

- **Metal hydroxides** are formed by the addition of alkaline reagents (lime or sodium hydroxide). Precipitation is then initiated by adjusting pH to the optimum level for the particular metal ion. Maintaining pH levels within a relatively narrow optimum range is usually necessary to achieve adequate metal precipitation. Pretreatment with oxidizing or reducing chemicals (e.g., hydrogen peroxide, ferrous sulfate) may be necessary to precipitate some metals (e.g., iron, manganese, chromium) in their least soluble form. Natural organic matter can inhibit the formation of insoluble metal hydroxides by forming metal-organic complexes. Metal hydroxide precipitation is typically effective for arsenic, cadmium, chromium (+3), nickel, zinc, manganese, copper (+2), tin (+3), and iron (+3).

- **Metal sulfides** are formed by the addition of either soluble sulfides (e.g., hydrogen sulfide, sodium sulfide, or sodium bisulfide) insoluble sulfides (e.g., ferrous sulfide). Sodium sulfide and sodium bisulfide are most commonly used. Sulfur dioxide and sulfur metabisulfite have also been demonstrated for chromium reduction prior to precipitation. Metal sulfides have lower solubilities than metal hydroxides, and effective metal removal efficiencies can be achieved over a broader pH range. The method is mainly used to remove mercury and lead and may be used to remove arsenic, cadmium, chromium (+3,or +6), silver and others. Sulfide precipitation also can be used to treat filtered ground water after hydroxide precipitation.

Appendix D5: Chemical Precipitation (continued)

Alternative Techniques/Enhanced Methods

- **Metal carbonates** are formed by the addition of calcium carbonate or by adding carbon dioxide to metal hydroxides. Solubilities of metal carbonates are intermediate between the solubilities of metal hydroxides and metal sulfides. Insoluble metal carbonates are easily filtered from treated ground water. The method is particularly good for precipitating lead, cadmium, and antimony.

- Sodium xanthate has shown promise as a precipitation agent similar to sodium sulfide.

Pre/Post-treatment

- Pretreatment to adjust pH is normally required to obtain the lowest precipitate solubility.

- Pretreatment may be necessary to oxidize iron or manganese compounds or reduce hexavalent chromium compounds into forms that can be readily precipitated.

- Depending on discharge requirements, the aqueous effluent may need pH adjustment and/or further polishing. Activated alumina or ion exchange media are regenerable treatment options for effluent polishing for metals. Activated carbon also may be used but spent carbon may require treatment and disposal as a hazardous waste.

- The sludge may require stabilization treatment by addition of lime/fly ash or portland cement to reduce permeability and the leachability of metals prior to disposal. In some cases, metals may be recovered from the residue for reuse, but this is generally not economical.

Selected References

Monopoli, A.V. 1993. Removing dissolved inorganics from industrial wastewater. *The National Environmental Journal:* 52-56.

U.S. Environmental Protection Agency. 1987. *Handbook on Treatment of Hazardous Waste Leachate.* EPA/600/8-87/006. Office of Research and Development, Cincinnati, OH. pp. 44-45.

U.S. Environmental Protection Agency. 1990. *CERCLA Site Discharges to POTWs Treatability Manual.* EPA/540/2-90/008. Office of Emergency and Remedial Response. PB91-921269/CCE. NTIS, Springfield, VA. pp. 11-23 to 11-36.

U.S. Navy. 1993. *Precipitation of Metals from Ground Water.* NEESA Document Number 20.2-051.6. Navy Energy and Environment Support Activity. Port Hueneme, CA. 11 pp.

Appendix D6: Ion Exchange/Adsorption

Ion exchange removes metal contaminants from water by passing contaminated ground water through a granular solid or other porous material, usually an impregnated resin, that exchanges sorbed ions (e.g., H^+, OH^-, Na^+, Li^+, CO_3^{--}) for contaminants dissolved in ground water. The ion exchange media are selected to have sorptive affinity for the ionic forms (cation or anion) of the contaminants being removed. The ion exchange media can therefore be either cationic, anionic, or a mixture of the two. Because ion exchange is a reversible process, resins can be regenerated by backwashing with a regeneration solution (e.g., brine; strong or weak acids or bases). Conventional ion exchange resins are generally too costly for large-scale ground-water treatment and are predominantly used for polishing of aqueous effluents after other treatment processes.

Applicability

Ion exchange is *applicable* to ionic contaminants such as dissolved metals or nitrates. Ion exchange is *not applicable* to non-ionic contaminants such as most organic compounds.

Contaminant Fate

Contaminants are removed from ground water through sorption onto the exchange media. When most of the exchange sites of the media become filled, the exchange media are regenerated by backflushing with a suitable regeneration solution. The concentrated backflush solution must then be disposed of or stripped of its contaminants. Exchange resins can generally be regenerated many times and have a relatively long useful life.

Design

Various resin types are available to tailor systems to discrete ionic mixes. For example, acid exchangers replace cations in water with hydrogen ions and base exchangers replace anions with hydroxide ions. Weak acid and base exchangers are selective for more easily removed ions while strong acid and base exchangers are less selective, removing most ions in the ground water. Generally, ease of cation and anion removal follows an affinity sequence specific to the ions in question. Synthetic resins are available with unique selectivity sequences. The wide variety of resins and other ion exchange media (e.g., activated alumina, biological materials) that are available make the selection of an appropriate exchange media a critical design step. Information on the applicability of specific resins may be obtained from resin manufacturers. In addition, ion exchange resins generally have an optimum pH range for effective metals removal. pH control may be required to achieve maximum removal efficiency from ground water.

A typical ion exchange installation has two fixed beds of resin. While one is in operation, the other is regenerated. Batch, fixed column, and continuous column bed designs can be used. Downflow column designs are generally preferred. Continuous column systems eliminate the need for backwashing but are not commonly used because of the complexity of the resin removal mechanics.

Flow rates up to 7,000 gpm have been reported for ion exchange systems. However, conventional ion exchange is generally cost-effective for ground-water treatment only at low flow rates or low contaminant concentrations. It is therefore primarily used as a polishing step following chemical precipitation or other treatment.

Appendix D6: Ion Exchange/Adsorption (continued)

Alternative Techniques/Enhanced Methods

- Activated alumina is an anionic exchange medium comprised of granulated, dehydrated aluminum hydroxide. Activated alumina is effective for removing fluoride, selenium, chromium (+6), and arsenic ions, which are exchanged for hydroxide ions. Adjustment of pH may be necessary to achieve optimal removal efficiency. The alumina is regenerated with a sodium hydroxide solution.

- Biological materials (e.g., algae, crop residues) have recently shown great promise as an innovative ion exchange media for metals. Biological media are significantly less costly than conventional resins (cents per pound vs. dollars per pound), and may become more commonly used for metals removal from ground water.

- Electrodialysis uses alternately placed cation and anion permeable membranes (made of ion exchange resin) and an electrical potential to separate or concentrate ionic species.

- Activated carbon adsorption can also be used to remove inorganics at low concentrations. **However, activated carbon is not identified as a presumptive technology for removal of metals dissolved extracted ground water.** Spent carbon used for metals removal can be difficult to regenerate and may require treatment and/or disposal as a hazardous waste.

Pre/Post-treatment

- Pretreatment may be required to remove suspended solids at concentrations greater than about 25 mg/L or oil at concentrations greater than about 20 mg/L. Large organic molecules also can clog resin pores and may need to be removed.

- pH adjustment may be necessary to achieve optimal metals removal.

- The backwash regeneration solution must be treated to remove contaminants.

- Post-treatment of spent ion exchange media may be required to recover concentrated contaminants or management as a hazardous waste may be required.

Selected References

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Appendix D7: Electrochemical Methods

Electrochemical processes use direct electrical current applied between two immersed electrodes to drive chemical oxidation-reduction reactions in an aqueous solution. Historically, electrochemical processes have been used to purify crude metals or to recover precious metals from aqueous solutions. Positively charged metal ions are attracted to the negatively charged electrode (the cathode), where they are reduced. The reduced metals typically form a metallic deposit on the cathode. Negatively charged ions are attracted to the positively charged electrode (the anode), where they are oxidized.

For contaminated ground water treatment, electrochemical cells have been used for the reduction (and subsequent precipitation) of hexavalent chromium to trivalent chromium. In this process, consumable iron electrodes are used to produce ferrous ions (Fe^{2+}) at the anode and hydroxide ions (OH^-) at the cathode. An oxidation-reduction reaction then occurs between the ferrous, chromium, and hydroxide ions to produce ferric hydroxide $Fe(OH)_3$ and chromic hydroxide $Cr(OH)_3$, which subsequently precipitate from solution.

Applicability

Electrochemical processes are *applicable* to dissolved metals. It is most commonly used in ground water treatment for the reduction and precipitation of hexavalent chromium. The process also may be applicable to removing other heavy metals including arsenic, cadmium, molybdenum, aluminum, zinc, and copper ions. Electrochemical processes have also been used for the oxidation of cyanide wastes (at concentrations up to 10 percent). Electrochemical processes are *not applicable* to organic compounds or asbestos.

Contaminant Fate

Dissolved metals either deposit on the cathode or precipitate from solution. Precipitates form an inorganic sludge that must be treated and/or disposed of, typically in a landfill. Spent acid solution, which is used to periodically remove deposits formed on the electrodes, will also require proper treatment and disposal. Cyanide ions are hydrolyzed at the anode to produce ammonia, urea, and carbon dioxide.

Design

Electrochemical reactors generally operate at ambient temperatures and neutral pHs. Both batch reactors and continuous flow reactors are commercially available. A typical electrochemical cell for hexavalent chromium reduction consists of a tank, consumable iron electrodes, and a direct current electrical supply system. An acid solution is used to periodically clean the iron electrodes, which need to be replaced when they are significantly consumed. Reactor residence times required for treatment depend on the contaminants present as well as the degree of mixing and current density. Reduction of hexavalent chromium generally requires short residence times (approximately 10 seconds), whereas treatment of cyanide compounds requires longer process times.

Pre/Post-treatment

- Pretreatment may be necessary to remove suspended solids.

- Settling or clarification post-treatment may be necessary to remove the precipitated trivalent chromic and ferric hydroxides formed during hexavalent chromium electrochemical reduction.

Appendix D7: Electrochemical Methods (continued)

Pre/Post-treatment (continued)

- The sludge may require stabilization prior to disposal by addition of lime/fly ash or portland cement to reduce permeability and metal leachability. In some cases, metals may be recovered from the plated electrode or precipitated residue, but this is generally not economical for typical ground-water applications.

Selected References

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Appendix D8: Aeration of Background Metals

Aeration (contact with air) removes some metals from water by promoting chemical oxidation and the formation of insoluble hydroxides that precipitate from the water. Aeration for metals removal differs from air stripping in that precipitation rather than volatilization is the desired effect of the technology.

Applicability

Aeration techniques are useful for the removal of limited number of dissolved cations and soluble metal compounds. This method is well suited for the removal of background metals such as iron and manganese which is necessary as part of a selected remedy such as pretreatment to air stripping. Methods of aeration for metals include aeration tanks, aeration basins, or cascade aeration. Aeration methods are usually not sufficient as an independent technology for iron and manganese, but are utilized as a step in the treatment process. Often, the air-water contact in tank and cascade aeration is not enough to obtain high removal efficiencies. Spray basins are limited by area, wind, and ice particle formation (Nyer, 1985).

Contaminant Fate

Dissolved metals are oxidized to insoluble hydroxides which precipitate from solution, and can then can be subsequently removed by flocculation, sedimentation, and/or filtration.

Design

The three types of aeration systems:

- Aeration tanks bubble compressed air through a tank of water.

- Cascade aeration occurs when air is made by turbulent flow and agitation.

- Spray or aeration basins use an earthen or concrete basin with a piping grid and spray nozzles that spray the water into the air in very fine droplets.

Related methods include aeration used to remove volatile organic contaminants from water are considered to be a type of air stripping, as discussed in Section 2.1.1. The use of aeration to promote aerobic biological treatment processes is considered to be an element of biological treatment as discussed in Section 2.1.4.

Pre/Post Treatment

- Aeration is often a pretreatment for other remediation technologies, such as air stripping, to remove certain metals.

- Aeration can be followed by other treatments such as flocculation, sedimentation, and/or filtration to remove oxidized metals.

Appendix D8: Aeration of Background Metals

Selected References

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